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HYDROGEN-BONDED SUPRAMOLECULAR ARRAY IN THE CRYSTAL STRUCTURE OF ETHYL 7-HYDROXY-2-OXO-*2H*-CHROMENE-3-CARBOXYLATE MONOHYDRATE

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ABSTRACT

The crystal structure of ethyl 7-hydroxy-2-oxo-*2H*-chromene-3-carboxylate monohydrate (**1**), $C_{12}H_{10}O_5.H_2O$, was established by X-ray crystallographic analysis. The molecule of the title compound is essentially planar except for the carboxylate substituent group. The crystal packing supramolecular array arises from hydrogen bonds and intermolecular C-H···O=C contacts of the organic molecules and solvent water molecules, with graph-set descriptor $R_4^2(8)$, $R_1^2(6)$, $R_4^4(20)$ and $C(5)$ motifs. The water molecules are involved as donors and acceptors. The hydrogen bond and intermolecular interaction network is reinforced by stacking of the sheet through π-π interactions.

Keywords: Crystal structure, Coumarins, X-ray diffraction

INTRODUCTION

The coumarins, compounds that occur naturally in many plant families, play an important role in organic chemistry. These compounds have been tested in a wide range of pharmacological models, and many derivatives have potentially useful biological activities among which are: antimicrobial, antithrombotic, anti-inflammatory, antimutagenic, antitumor, and enzyme inhibitory (cyclooxygenase, lipoxygenase, and monoamine oxidase).[1-4] In addition to their broad biological interest, the coumarins are sometimes colored and generally exhibit intense fluorescence, which has attracted interest for the development of new technological applications in areas such as liquid crystals for use in photoelectronic devices.[5] In the present study, an X-ray analysis of ethyl 7-hydroxy-2-oxo-*2H*-chromene-3-carboxylate monohydrate (**1**) was performed in order to determine its inherent conformation and describe the crucial role of hydrogen bonds to water and weak intermolecular interactions in the assembly of its supramolecular architecture.

EXPERIMENTAL

Synthesis

Ethyl 7-hydroxy-2-oxo-*2H*-chromene-3-carboxylate monohydrate was synthesized in two steps. First, resorcinol was formylated (Vilsmeier-Haack),[6] and subsequently condensed with ethyl malonate (Knoevenagel) and cyclized in a single step.[7] The solid was recrystallized in EtOH (5.6 g, 52%) to afford aggregates of yellow prisms (Scheme 1).

Scheme 1. Reagents and conditions: (a) $POCl_3$, DMF, ACN, 2 h; (b) piperidine, AcOH, EtOH, reflux, 6 h.

Refinement

H atoms attached to C3, O3 and O1W were located in a Fourier map and their positions and isotropic displacement parameters were refined freely. All other H atoms were positioned geometrically and constrained to ride on their parent atoms (C—H: 0.93–0.97 Å). Displacement factors were taken as U_{iso}(H) = kU_{eq}(C); k = 1.2–1.5. The crystal data, data collection and refinement are summarized in Table 1.

Computing details

Data collection: Bruker *SMART* (BRUKER 1996); cell refinement: Bruker SAINTPLUS V6.02 (BRUKER 1997); data reduction: Bruker *SHELXTL* V6.10 (BRUKER 2000); program used to solve structure: *SHELXS97* (Sheldrick, 1990); program used to refine structure: *SHELXL97* (Sheldrick, 1997).[8-9] Molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *PLATON* (Spek, 2003).[10, 11]

Table 1. Crystal data and details of the structure determination for compound **1**.

Crystal data	
$C_{12}H_{10}O_5.H_2O$	δ = 99.388(5) º
Mr = 252.22	V = 583.3(2) Å^3
Triclinic, P-1 (Nº 2)	Z = 2
a = 6.7177(17) Å	Mo*Ka* radiation
b =7.2637(18) Å	m = 0.117 mm^{-1}
c =12.618(3) Å	T = 298 K
α = 104.064(4) º	0.32 x 0.14 x 0.05 mm
β = 95.506(5) º	
Data collection	
Bruker SMART CCD diffractometer	1057 reflections with $I > 2\sigma(I)$
4269 measured reflections	R_{int} = 0.043
2035 independent reflections	
Refinement	
R [(F^2> 2σ (F^2)] = 0.040	H atoms treated by a mixture of independent and constrained refinement
*w*R(F^2) = 0.062	180 parameters
S = 0.96	$\Delta\rho_{max}$ = 0.15 e Å^{-3}
2035 reflections	$\Delta\rho_{mim}$ = -0.15 e Å^{-3}

RESULTS AND DISCUSSION

The asymmetric unit of the title compound (**1**) consists of one $C_{12}H_{10}O_5$ organic molecule and one solvent water molecule. A perspective view of the molecular structure with the atom labels is depicted in Figure 1. A search in the Cambridge Structural Database (CSD version 5.31, August 2010) of coumarin

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and derivates revealed the regioisomer ethyl 7-hydroxy-4-coumarinacetate (**2**) [CSD refcode SICREB (Subramanian et al. 1990)] and 7-hydroxy-4-coumarinacetic acid monohydrate (**3**) [CSD refcode SICRIF (Sivakumar et al. 1990)].[12,13] Selected bond lengths and angles of molecule **1** with their estimated standard deviations (esd`s) are given in Table 2.

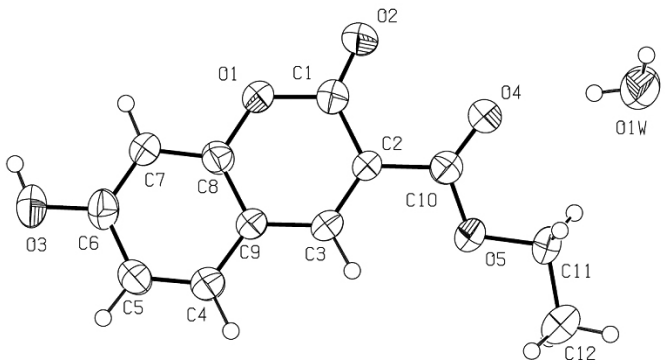
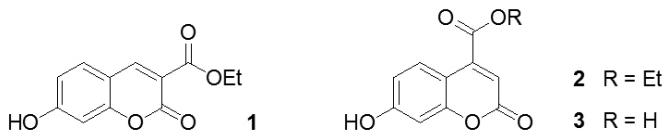


Figure 1. The structure of **1** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius.

Table 2. Selected geometric parameters (Å, º)

O1-C1	1.395 (2)	C2-C3-C9	122.2 (2)
C4-C5	1.368 (3)	C7-C8-C9	123.1 (2)
O3-C6	1.349 (2)	C8-O1-C1-C2	0.9 (3)
C11-C12	1.508 (2)	C3-C2-C10-O4	−162.9 (2)
C3-C2-C10	121.69 (19)	C11-O5-C10-O4	2.6 (3)
C2-C3-C9	120.8 (2)	C10-O5-C11-C12	−178.85 (18)

The molecule (**1)** is essentially planar except for the carboxylate substituent group at C2 with a C3-C2-C10-O5 torsion angle of 16.1(3)º. The torsion angles C2-C3-C10-C11 of the corresponding substituent (at C3: ethoxycarbonylmethyl in **2** and acetic acid residue in **3**), are -97.7(3)º and 103.6(3)º, respectively. The C2=C3 bond distances in **1** [1.353(3) Å] and in **2** [1.358(4) Å] are similar. However, the bond distance in **3** [1.341(4) Å] is shorter than in **1** and **2**, which can be attributed to the acetic acid moiety. All the other relevant structural parameters (bond distances and angles) are as expected and in acceptable agreement with the recently described analogues (Table 2).



The three-dimensional supramolecular architecture of compound **1** can be analyzed in terms of various components such as motifs, chains and stacking interactions. The crystal structure of **1** is assembled from the $C_{12}H_{10}O_5$ molecules with solvent water molecules *via* hydrogen-bonding interactions. Hydrogen bonds, π-π interactions and weak intermolecular contacts are responsible for the crystal packing.[14-17] In the asymmetric unit, two water molecules are related forming an inversion centre. The two water molecules serve to link four $C_{12}H_{10}O_5$ molecules forming a two-dimensional array running parallel to the [010] plane (Figure 3). The water molecules are involved as hydrogen bond donors and acceptors. Each water molecule acts as a single acceptor, in an O-H···OW hydrogen bond, and as a triple donor forming a two-center H1W···O=C bond and single-center H2W···O=C bond (Table 3). The central core constitutes a graph-set descriptor $R_4^2(8)$ motif (Figure 3b).[17-19]

Table 3. Hydrogen-bond and intermolecular contact interaction geometry (Å, º).

D-X...A	d(D-X)	d(X...A)	d(D...A)	<(DXA)
O1W-H1W···O2^{i}	0.81 (3)	2.24 (3)	2.876 (3)	135 (3)
O1W-H1W···O4^{i}	0.81 (3)	2.26 (3)	2.963 (3)	145 (3)
O1W-H2W···O4^{ii}	0.85 (3)	2.13 (3)	2.976 (3)	174 (3)
O3-H3B···O1W^{iii}	0.85 (2)	1.81 (3)	2.648 (3)	170 (3)
C3-H3···O2^{iv}	0.976 (15)	2.534 (16)	3.452 (3)	156.7 (13)

Symmetry code : (i) 2-x,1-y,1-z, (ii) x,y,z , (iii) x,y,z-1, (iv) x-1,y,z

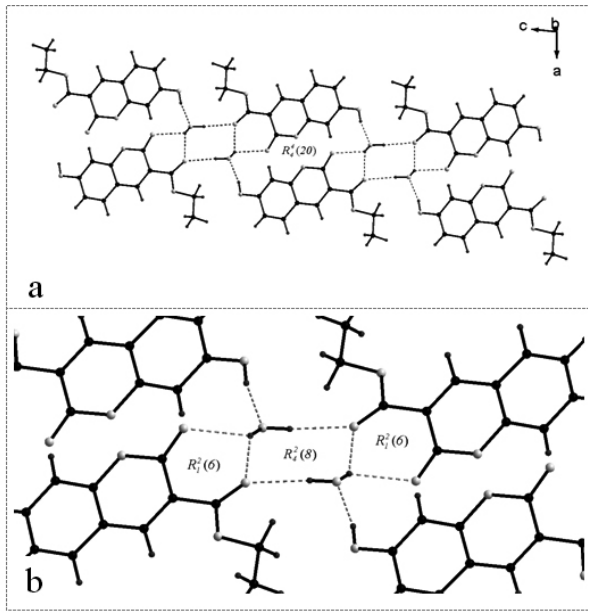


Figure 3. A partial packing of the crystal structure of **1:** (**a**) A view of the formation of a hydrogen-bonded sheet running parallel to the *ac* plane. (**b**) A view of the hydrogen bonds in the central core linking the components into centrosymmetric six-molecule aggregates consisting of two water molecules and four $C_{12}H_{10}O_5$ molecules. Dashed lines represent hydrogen bonds.

The hydrogen bonds of the water molecules that are involved in the two-donor centers H1W···O=C generate two graph-set descriptor $R_1^2(6)$ motifs (figure 3b). This graph-set is formed by the linkage of water bonds, O1W-H1W···O2 [symmetry code: 2-x,1-y,1-z] and O1W-H1W···O4 [symmetry code: 2-x,1-y,1-z], with both O=C carbonyl groups of one molecule (Table 3). Besides, these two-dimensional sheets are additionally stabilized by the combinations of two O3-H3B···O1W and two O1W-H1W···O2 hydrogen bonds. The links of two water molecules with two $C_{12}H_{10}O_5$ molecules generate a graph-set descriptor $R_4^4(20)$ motif in the *ac* plane (Figure 3a). [17-19]

The crystal packing structure contains chains that run along the crystallographic *a*-axis generated by intermolecular C-H···O=C contacts (Table 3). The H···O contact distance is 2.543 (15) Å and the C···O distance is 3.452 (3) Å, both within the C–H···O distance and angle range.[18-19] The intermolecular C3-H3···O2 [-1+x,y,z] interactions form a graph-set descriptor $C(5)$ motif (Figure 2). The packing structure contains an additional weak intermolecular contact O1···H4 [1+x,y,z] with a bond distance of 2.62(2) Å and an angle of 113.4(4)º.

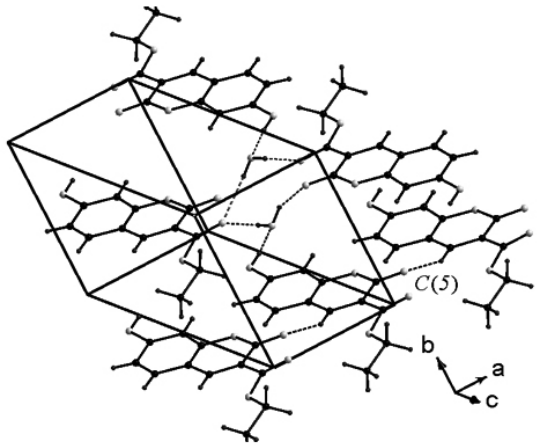


Figure 2. Part of the crystal structure of **1** showing the C-H···O=C chain running along the *a*-axis and graph-set descriptor $C(5)$ built from C3-H3···O2 [symmetry code:-1+x,y,z]. Dashed lines represent intermolecular interactions.

The sheets are packed to form a three-dimensional network *via* π-π interactions between parallel stacked coumarin rings, C1-C3/O1/C8-C9 (centroid *Cg1*) and C4-C9 (centroid *Cg2*). The perpendicular *Cg1*···*Cg2* distance is 3.5688 (15) Å (Figure 3). A similar packing interaction has been observed in the crystal structure of cinnamyl 2-oxo-2*H*-chromene-3carboxylate [centroid-centroid distance of 3.8380 (15)Å].[20]

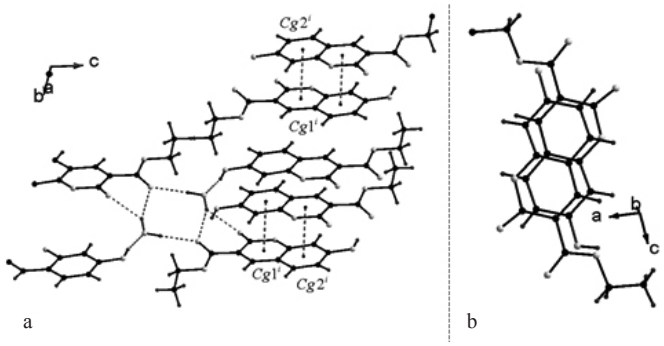


Figure 3. A partial packing view of the crystal structure of **1** showing the formation of weak intermolecular contacts between *Cg1*...*Cg2* [symmetry code (i): 1-x,1-y,-z] in the *bc*-plane (**a**). The centroids *Cg* are denoted by small black spheres and dashed lines represent intermolecular interactions. (**b**) Shows parallel stacking between neighboring coumarin rings in the *ac* plane.

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Supplementary Information: Crystallographic data (excluding structure factors) for the structural analysis have been deposited in the Cambridge Crystallographic Data Centre, CCDC 801740. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre; Postal Address: CCDC, 12 Union Road, Cambridge CB21EZ, UK, Telephone: (44) 01223 762910, Fax: (44) 01223 336033, e-mail: deposit@ccdc.cam.ac.uk.

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